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Removal of Anionic Surfactants in Detergent Wastewater by Chemical Coagulation

[1]Amir Hossein Mahvi, [2]A. Maleki and [2]B. Roshani
[1]Department of Environmental Health Engineering, Center for Environmental Research,
Tehran University of Medical Sciences, Tehran, Iran
[2]Department of Environmental Health,
Faculty of Health, Kurdistan University of Medical Sciences, Sanandaj, Iran

Abstract: The present study was conducted to investigate the treatment of surfactant wastewater by a bench scale physical-chemical treatment. Experiments were conducted to examine the effects of pH and amount of coagulant on the surfactant removal. The result of the wastewater characterization showed that the concentration of the organic matter were high, expressed as COD, in the range of 4920 mg L^{-1}, while the biodegradable portion was low. These values indicate that organic compounds are not easily subjected to biological treatment. In addition, methylene blue active substance appeared high concentration as well as total solids and turbidity. The experiments for the treatment of the wastewater were performed using various chemicals such as lime, alum and ferric chloride. The use of lime gave 21 and 17%, COD and MBAS removal, while by using alum a slightly higher was achieved, 37 and 28%, respectively. The use of ferric chloride led to a 89% COD removal and a 80% surfactant removal.

Key words: Surfactant removal, detergent wastewater, coagulation

INTRODUCTION

Detergents are formulations designed to have cleaning/solubilisation properties. These formulations consist of surface-active agents (surfactants) to gather with subsidiary components including builders, boosters, fillers and auxiliary compounds[1]. The active matter of detergents is composed of natural and/ or synthetic surfactants of different types[1]. The groups normally used are the anionic and nonionic surfactants. Alkylbenzene Sulfonte (ABS) and Linear Alkylbenzene Sulfonate (LAS) are the most frequently employed synthetic surfactant[2]. The large scale usage of detergents and increasing public concern over environmental issues has stimulated a widespread interest among detergent manufacturers, regulatory agencies and consumers, in understanding the behavior of detergent chemicals in the environment[3].

Because one of the principal route of surfactant disposal is by wastewater treatment, it is important to understand the mass flow and changing composition of surfactants as they pass through wastewater treatment facilities. Wastewater treatment play an important role in the life cycle of surfactants by reducing the mass flow of surfactants to the environment, by altering the composition of surfactants mixtures and by acting as point sources of surfactants in aquatic environments[3].

The main sources of wastewater produced in plants manufacturing toiletries and detergents are the washing processes. The polluting load of this wastewater is, mainly, due to the residual product in the reactor which has to be washed away in order to use the same facility for the manufacture to other products. The extreme diversity of raw materials and production schemes employed by the industries in reflected in the variety and complexity of this type of wastewater. As a result, the industries pose problems in assessing effluent characteristics and subsequently defining pollution control technologies[4]. The high and varied polluting load of the detergent wastewater can cause significant environmental problems[5-8]. Prior to its disposal in the environment an efficient treatment process must be applied. Due to its complexity detergent wastewater is very difficulty to treat[4]. In the literature, limited data have been reported on the removal of polluting load from this type of wastewater[4,8].

This study is an extensive research referring to detergent wastewater. For this particular work a chemical method was applied in order to reduce the detergent concentration of the wastewater. This can be achieved by the destabilization of colloids which can be brought about by processes such as precipitation, coagulation and

Corresponding Author: Dr. Amir Hossein Mahvi, Department of Environmental Health Engineering,
Centre for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran
E-mail: ahmahvi@yahoo.com

flocculation and finally the comparison between the removal efficiency of detergent and organic load by three types of chemicals.

MATERIALS AND METHODS

The treatment of detergent wastewater samples by coagulation/flocculation and precipitation was examined systematically using a jar test apparatus. Wastewater samples were taken from a local plant manufacturing detergents. The samples were collected in glass bottles washed with a sulphochromic mixture and they were properly preserved and kept refrigerated during experimentation. Chemical characterization was performed by determining the following parameters: pH, Turbidity, Methylene Blue Active Substances (MBAS) and Chemical Oxygen Demand (COD). The surfactant concentration was determined by standard methods using a uv/vis spectrophotometer (uv/vis spectrophotometer 21 D-Mitonoy). The turbidity was measured using a turbid meter (2100P turbid meter, HACH)[9].

Experimental procedures: At the first, the optimum pH value for everyone of coagulant was established by a series of experiments using different wastewater samples with initial pH ranging from 3-13. Then, the optimum lime [Ca $(OH)_2$]dose was established by a series of experiments using different wastewater samples with optimum pH range (pH=11). The lime and the wastewater were vigorously mixing for 1 min at a speed of 100 rpm, followed by slow mixing for 10 min at a speed of 40 rpm and then allowed to settle for 30 min. Samples of the clarified wastewater were taken for determination of surfactant concentration, turbidity and the effectiveness of the method for COD removal.

Similar tests were performed using alum [$Al_2(SO_4)_3$. 18 H_2O]. In particular, different wastewater samples with initial pH in the range of 8 were treated by alum and its optimum dose was established. Also, similar tests were performed using ferric chloride with optimum pH (pH=12) to establish of optimum dose of ferric chloride.

RESULTS AND DISCUSSION

The pH value of the wastewater showed very high value about 11 (Table 1). The total solids were in high concentration about 9920 mg L^{-1}. The organic load concentration were very high since the COD was in the range of 4550 mg L^{-1}, while its biodegradable portion was low since the BOD was in the range of 1890 mg L^{-1}. These values indicate that organic compounds are not easily subjected to biological treatment. In addition, methylene blue active substances appeared in concentration of 430 mg L^{-1}. As a result the wastewater quality, which depends on the production process applied, varies significantly (Table 1).

In this study, experiments were performed using various chemicals such as lime, alum and ferric chloride, in order to examine their ability to remove the organic compounds from the wastewater.

Having found the optimum pH values (pH=11) at which precipitation can occur with lime (Fig. 1), a series of experiments were performed in other to find the optimum lime dose, expressing the results as COD, MBAS and turbidity percentage removal. Figure 2, 7 and 8 indicate that the lime dose for the maximum COD, turbidity and MBAS removal, about 21, 87 and 17%, respectively, is 500 mg L^{-1}.

Similar to lime, jar tests were carried out using alum and ferrous chloride. It is found that optimum pH value 8 and 12 for alum and ferric chloride, respectively (Fig. 3 and 5). A similar series of experiments were performed in order to find the optimum alum and ferric chloride dose. The results indicate that the alum dose for the maximum turbidity MBAS and COD removal about 91, 28 and 37%, respectively is 900 mg L^{-1} (Fig. 4, 7 and 8). Also, the results which are shown in Fig. 6-8 indicate that the ferric chloride dose for the maximum turbidity, MBAS and COD removal about 96, 80 and 89%, respectively, is 100 mg L^{-1}.

The pH effect on the flocculation/coagulation process has been shown in the previous studies to be quite significant[4,10]. Optimum pHs ranged 9-10, 5-8 and 10-11 had been observed by the other researchers for the

Table 1: Values of the wastewater characteristics

Parameters	Value	Unit
pH	11	
Total solids	9920	mg L^{-1}
Turbidity	320	NTU
COD	4550	mg L^{-1}
BOD	1890	mg L^{-1}
MBAS	430	mg L^{-1}

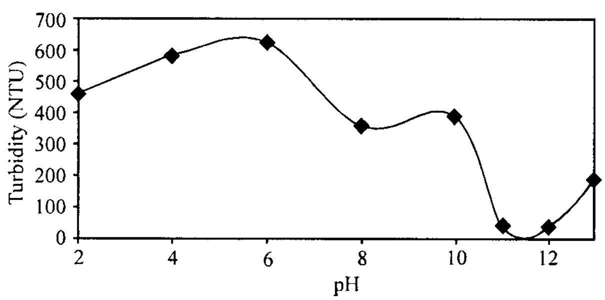

Fig. 1: Effect of pH on the coagulation of detergent wastewater with $Ca(OH)_2$, Lime dose= 500 mg L^{-1}

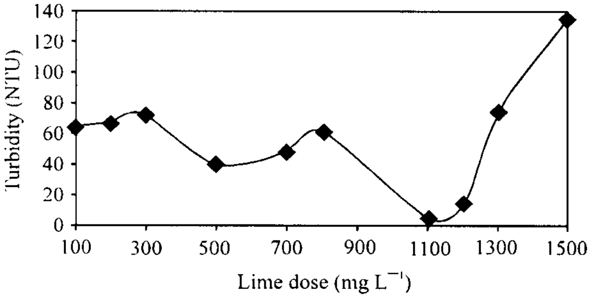

Fig. 2: Effect of lime dose on the turbidity removal in detergent wastewater, pH=11

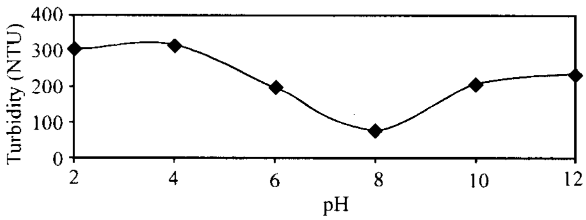

Fig. 3: Effect of pH on the coagulation of detergent wastewater with alum, Alum dose= 300 mg L^{-1}

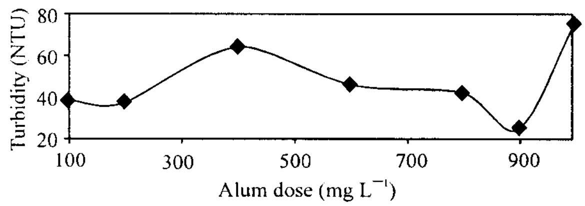

Fig. 4: Effect of alum dose on the turbidity removal in detergent wastewater, pH=8

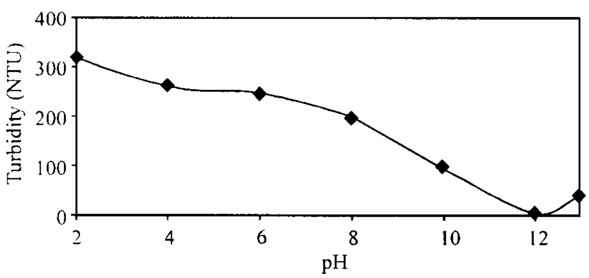

Fig. 5: Effect of pH on the coagulation of detergent wastewater with ferric chloride, Ferric chloride dose= 300 mg L^{-1}

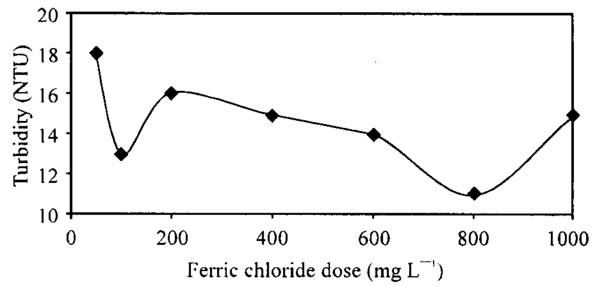

Fig. 6: Effect of ferric chloride dose on the turbidity removal in detergent wastewater, pH= 12

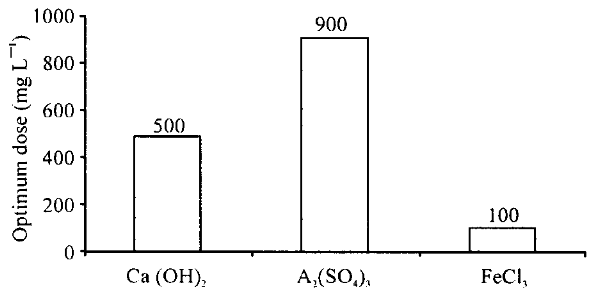

Fig. 7: Optimum dose of lime, alum and ferric chloride

coagulation process using alum, lime and ferric chloride. The similar optimum pHs were also obtained in this study. Hence, maintaining the pH and its optimum was adopted for all test runs.

The high value of turbidity (320 NTU) and total solid (9920 mg L^{-1}) of wastewater samples will increase the removal efficiency of surfactants. Thus, the amount of particulate matter should be considered in the detergent removal by coagulation. Due to their amphophilic nature surfactants in raw sewage can adsorb to the surface of resident particulate matter. Berna *et al.*[10] reported that a significant proportion of detergents (particular LAS) in raw sewage (10-35%) adsorb to particulate matter. Sediment removed from primary settling tanks is relatively rich in LAS, with concentrations ranging from 5000-15000 mg L^{-1} being reported[11]. The process of adsorption of surfactants to particulate matter is primarily driven by the hydrophobic effect and specific of electrostatic interactions[11,12].

Results indicate that the removal efficiency of COD and MBAS from wastewater by lime is low. Thus, the application of lime in removal of soluble pollutants is limited. Similar results were obtained by alum. Thus, for detergent wastewater treatment by using lime or alum, their combinations to gather or with other chemicals in order to find the most efficient treatment, are necessary. According to Papdopoulos *et al.*[4] the use of 1500 mg L^{-1} of lime gave COD removal ranging from 19-29%. It combination with 1500 mg L^{-1} alum improved COD removal up to 18%, leading to total COD removal of 33-47%. In another study by Hashim[8], the combination of 2200 mg L^{-1} alum with 1100 mg L^{-1} lime, gave COD, MBAS, TSS and turbidity removal in the range of 75, 93.7, 88.6 and 81.4%, respectively.

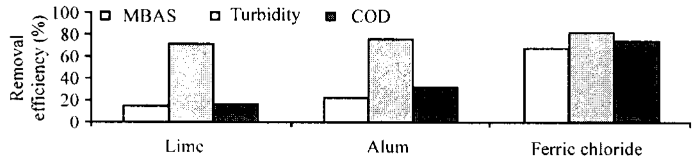

Fig. 8: Effect of lime, alum and ferric chloride on the removal efficiency of turbidity, detergent and COD

The higher removal rate of COD concentration, detergent and turbidity were found with addition of 100 mg L^{-1} ferric chloride. This investigation has shown that even without simultaneous addition of lime or other chemicals very good removal in the coagulation step can be achieved. Despite this, the treatment based on the addition of chemical did not give the require wastewater quality for its disposal in the environment.

During the coagulation, a large amount of detergent and COD in the wastewater was observed. Therefore biological treatment will not be applicable by itself. Of course the biological treatment has a high efficiency for treatment of detergent in wastewater in comparison with other methods. For example, LAS sorption to sewage sludge accounts 26%, while biodegradation removes 73%[1]. Thus although, the chemical coagulation is efficient for COD removal. But, it is inefficient for detergent removal. As a result, Hossaini[13] shown the removal efficiency of detergent by physical, chemical and biological treatment was 75, 6-36 and 68-90%, respectively. Hence, it is recommended, the elimination of the surfactants from wastewater is a combination of adsorption to primary and secondary sludge and biodegradation in aerobic treatment[14]. It should also be noted that at an abs and LAS concentration above 10 mg L^{-1}, foaming in the aqueous solution would be a sever problem[15].

A chemical coagulation was employed in the present study to treat the wastewater containing anionic surfactant. The results of this study show the wastewater examined under this study contained high organic loads of which the main portion was not biodegradable.

Therefore biological treatment will not be applicable by itself. The treatment employed, using lime, alum and ferric chloride gave a detergent removal of up to 17, 28 and 80%, respectively.

In conclusion, the total COD removal and detergent removal achieved by ferric chloride is quite satisfactory, taking into account the fact that the initial organic load concentrations were too high. Despite this, the treatment based on the addition of chemical did not give the required wastewater quality for its disposal in the environment. The polluting load can be significantly reduced be adjusting the production process and reducing the number of changes of products for a given reactor.

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